OLEOCHEMICALS FROM PALM OIL AND PALM KERNEL OIL

Keywords: Oleochemicals; Palm Oil; Palm kernel oil

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Oleochemicals are chemicals derived from natural oils and fats. The important basic oleochemicals, which are essentially the building blocks of the oleochemical industry, are fatty acids, methyl esters, fatty alcohols and fatty amines. These oleochemicals, together with their derivatives, have a large variety of end uses. The principal raw materials for the production of these oleochemicals are tallow and coconut oil. This situation is changing due to the growing importance of palm oil in the world oils and fats scene. Technically, palm oil and palm oil products could to a large extent replace tallow, while palm kernel oil and coconut oil are interchangeable raw materials in oleochemical manufacturing. The ASEAN region will be a significant area for the oleochemical industry as it is the largest palm oil and lauric oil producer.

INTRODUCTION

Fossil and historical evidences indicate that the oil palm, *Elaeis guineensis*, originated from West Africa, where it was used as a source of oil and Vitamin A for the local population. The main region of cultivation of the oil palm lies in the tropical rain-forest area

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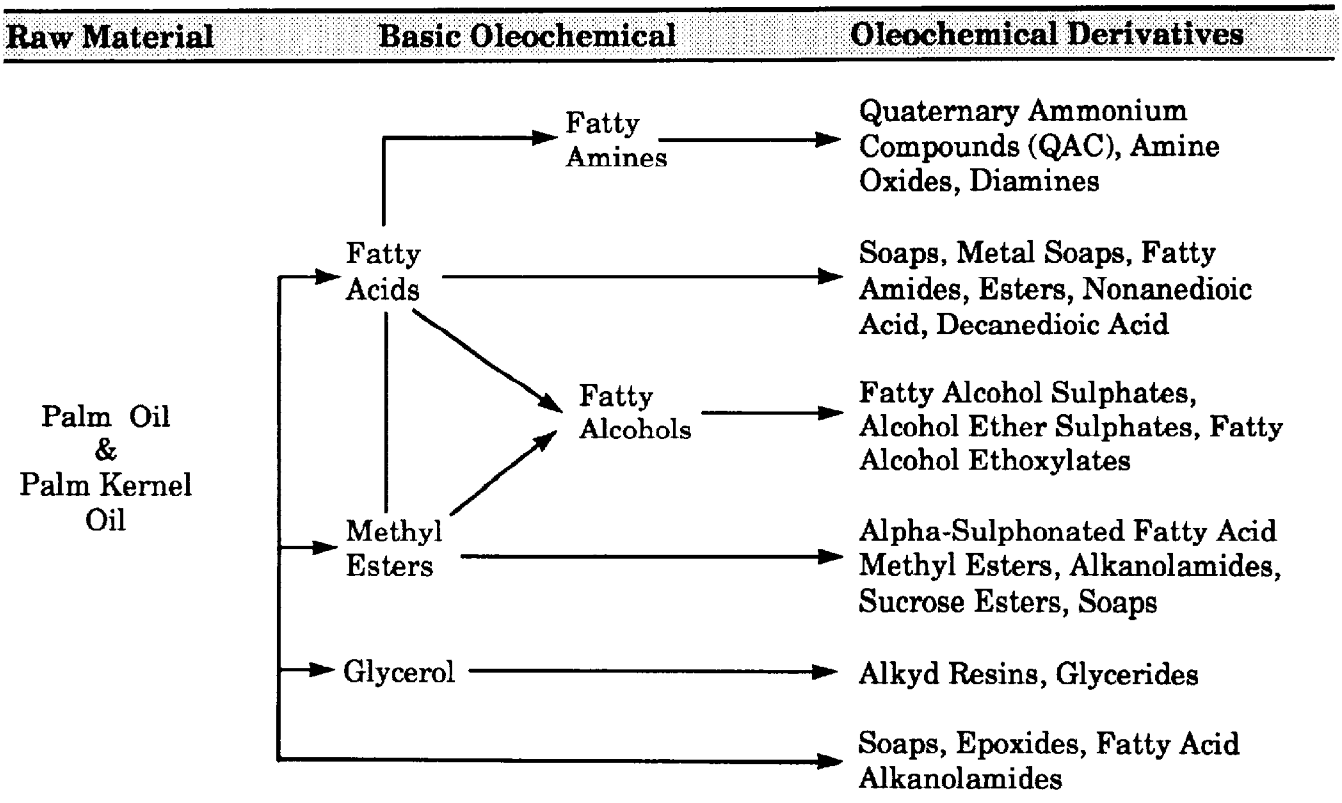

Figure 1.
Oleochemicals from palm oil and palm kernel oil

between 10° north and south of the equator. Today, the important countries for oil palm cultivation are Malaysia, Indonesia, Nigeria and Ivory Coast.

The oil palm fruit produces two types of oil, palm oil from the mesocarp and palm kernel oil from the nut, the endosperm. They are chemically different and have between them practically the entire range of long, medium and short chain fatty acids.

The world production of palm oil in 1987 was about 7 810 000 tonnes, together with 1 040 000 tonnes of palm kernel oil (Oil World Annual, 1988); 90% of the palm oil found its way into food products, leaving about 10% for non-food applications. The two main non-food uses are in the manufacture of oleochemicals and soaps.

Oleochemicals are chemicals derived from oils and fats; they can be divided into two groups of products, *i.e.* basic oleochemicals and oleochemical derivatives.

Basic oleochemicals are fatty acids, methyl esters, fatty alcohols and fatty amines with 1,2,3-propanetriol (glycerol) being an important by-product. They are essentially the building blocks of the oleochemical industry. From these basic oleochemicals a very wide range of oleochemical derivatives can be produced which have a large variety of end uses. *Figure 1* is a flow chart leading from palm oil and palm kernel oil to basic oleochemicals and their derivatives (Richtler *et al.*, 1984 and Hamirin *et al.*, 1985). Since palm oil and palm kernel oil contain between them almost the entire range of fatty acids, practically all the oleochemicals can be produced from them. However this paper will concentrate on the basic oleochemicals and some of their important derivatives which have been produced or

TABLE 1.
FATTY ACID COMPOSITION (%) OF PALM OIL AND PALM STEARIN COMPARED TO TALLOW

Fatty Acid	Palm Oil	Palm Stearin	Tallow
Dodecanoic C12:0	0.1 - 1.0	0.1 - 0.6	0 - 0.2
Tetradecanoic C14:0	0.9 - 1.5	1.1 - 1.9	2 - 8
Hexadecanoic C16:0	41.8 - 46.8	47.2 - 73.8	24 - 30
Hexadecenoic C16:1	0.1 - 0.3	0.05 - 0.2	2 - 3
Octadecanoic C18:0	4.2 - 5.1	4.4 - 5.6	14 - 25
Octadecenoic C18:1	37.3 - 40.8	15.6 - 37.0	40 - 49
Octadecadienoic C18:2	9.1 - 11.0	3.2 - 9.8	1 - 5
Others	0 - 1	0 - 1	0 - 1

have the potential to be manufactured from palm oil and palm kernel oil. 1,2,3-Propanetriol has been excluded because it has been dealt with at length in other papers.

RAW MATERIALS

The manufacture of oleochemicals uses a wide range of raw materials, from inedible to edible oils and fats. Among them tallow and coconut oils are the principal raw materials generally used. In 1980 palm oil and palm kernel oil accounted for less than one percent of the total amount of oils and fats used to make fatty acids and their derivatives: tallow and coconut oil accounted for about 68% and 20% respectively. The choice of raw material depends on the properties of the oils, availability and cost competitiveness (Santhiapillai, 1986).

Properties of Palm Oil and Palm Kernel Oil

The fatty acid compositions of tallow and coconut oils, together with those of palm oil, palm kernel oil and palm stearin are shown in *Tables 1* and *2* (Santhiapillai, 1986; Tan *et al.*, 1981; Tan *et al.*, 1981; Siew *et al.*, 1981). Palm stearin is the solid fraction obtained from fractionation of palm oil. The liquid fraction is palm olein. From *Tables 1* and *2* one can realize that there is a great possibility for inter-substitution among these fats and oils. Technically, therefore, palm oil and palm stearin could to a large extent replace tallow, and similarly palm kernel oil and coconut oil are interchangeable materials in oleochemical manufacturing. Palm oil and palm stearin have a higher hexadecanoic (palmitic) acid content than tallow. This could be an advantage for certain applications and a disadvantage for others.

However palm oil and palm stearin are recognized as vegetable oils; their derivatives and applications are fully acceptable to people for whom animal fats may be subject to religious taboos. As for palm kernel oil and coconut oil: palm kernel oil has a lower content of octanoic (caprylic) and decanoic (capric) acid than coconut oil. This is obviously a disadvantage

TABLE 2.
FATTY ACID COMPOSITION (%) OF PALM KERNEL OIL COMPARED TO COCONUT OIL

Fatty Acid	Palm Kernel Oil	Coconut Oil
Hexanoic C6:0	0.1 - 0.5	0 - 0.8
Octanoic C8:0	3.4 - 5.9	3 - 6
Decanoic C10:0	3.3 - 4.4	6 - 10
Dodecanoic C12:0	46.3 - 51.1	44 - 52
Tetradecanoic C14:0	14.3 - 16.8	13 - 19
Hexadecanoic C16:0	6.5 - 8.9	8 - 11
Octadecanoic C18:0	1.6 - 2.6	1 - 3
Octadecenoic C18:1	13.2 - 16.4	5 - 8
Octadecadienoic C18:2	2.2 - 3.4	0 - 3
Others	traces - 0.9	0 - 1

when these acids are in demand, but it is a distinct advantage in soap manufacture, where the octanoic and decanoic fatty acids are liable to cause skin irritation (Chen *et al.*, 1984, De Vries, 1984).

Availability of Palm Oil and Palm Kernel Oil

The production of palm oil and palm kernel oil has achieved a very impressive growth over the last ten years. During the period 1977 to 1987, palm oil production increased by about 136% and that of palm kernel oil by 97 per cent. Tallow and coconut oil production increased by only 8% and 9% respectively *(Figure 2)*. In 1987, the world production of palm oil was about 10.8% (7.8 million tonnes) of the total world production of oils and fats while palm kernel oil accounted for about 1.4% (1 million tonnes). In the same year, Malaysia produced about 60% and 54% of the total world output of palm oil and palm kernel oil respectively (Santhiapillai,1986; Wiese,1987; Santhiapillai, 1988).

This outstanding growth in production is expected to continue. By the year 2000, palm oil and palm kernel oil together are expected to represent about 20% of the world's total production of oils and fats. The increase is very dramatic by comparison with tallow and coconut oil *(Figure 3)*. In terms of export, palm oil is the world's leader. *Figure 4* shows the very striking increase in exports from. 1977 to 1987. Malaysia now accounts for about 80% of the total world export of palm oil and palm kernel oil, and this makes Malaysia the largest single exporter of oils and fats in the world (Santhiapillai 1988, Mielke, 1985).

Hence palm oil and palm kernel oil will become increasingly available at much faster

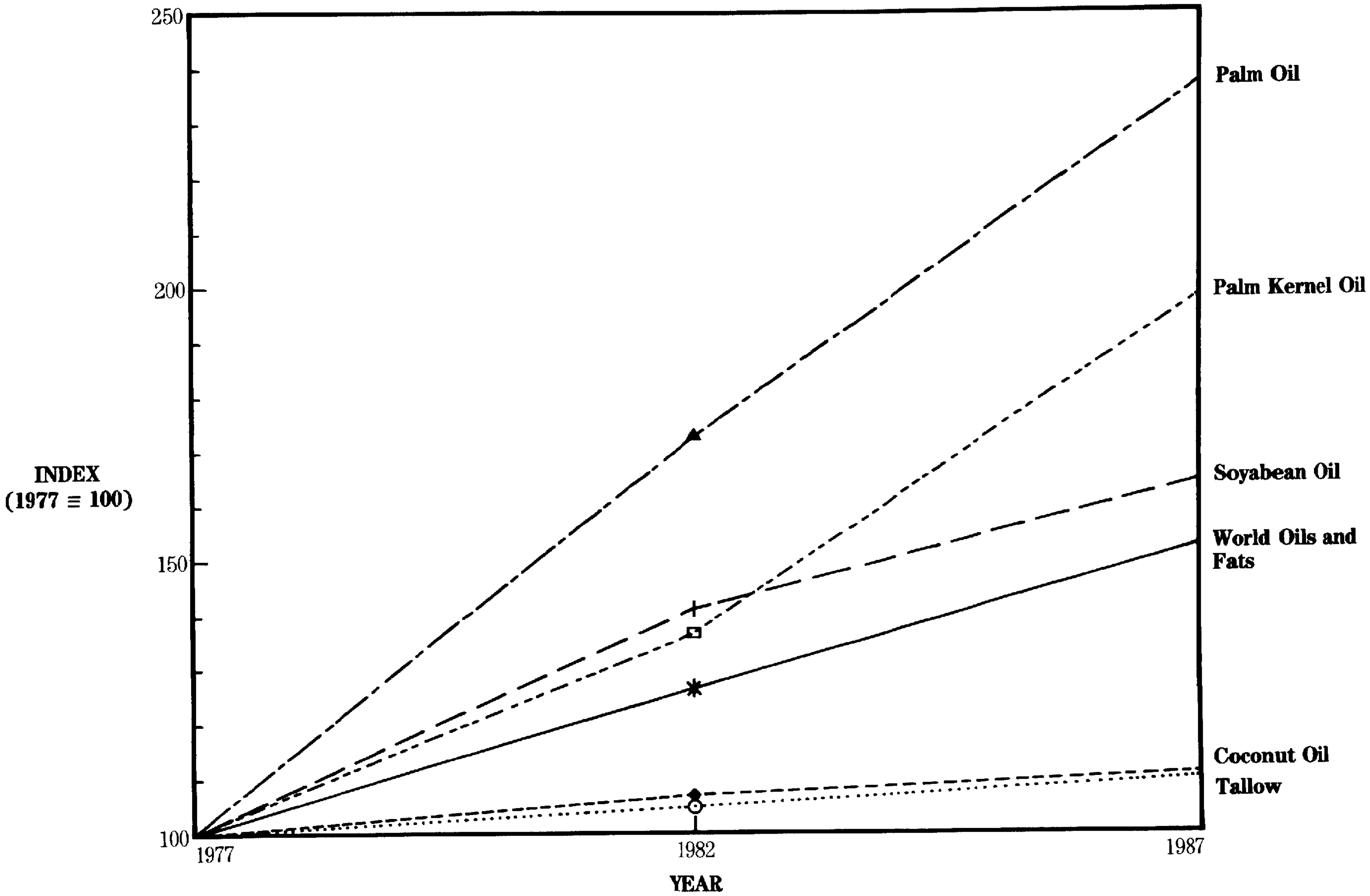

Figure 2.
World Production of Oils and Fats

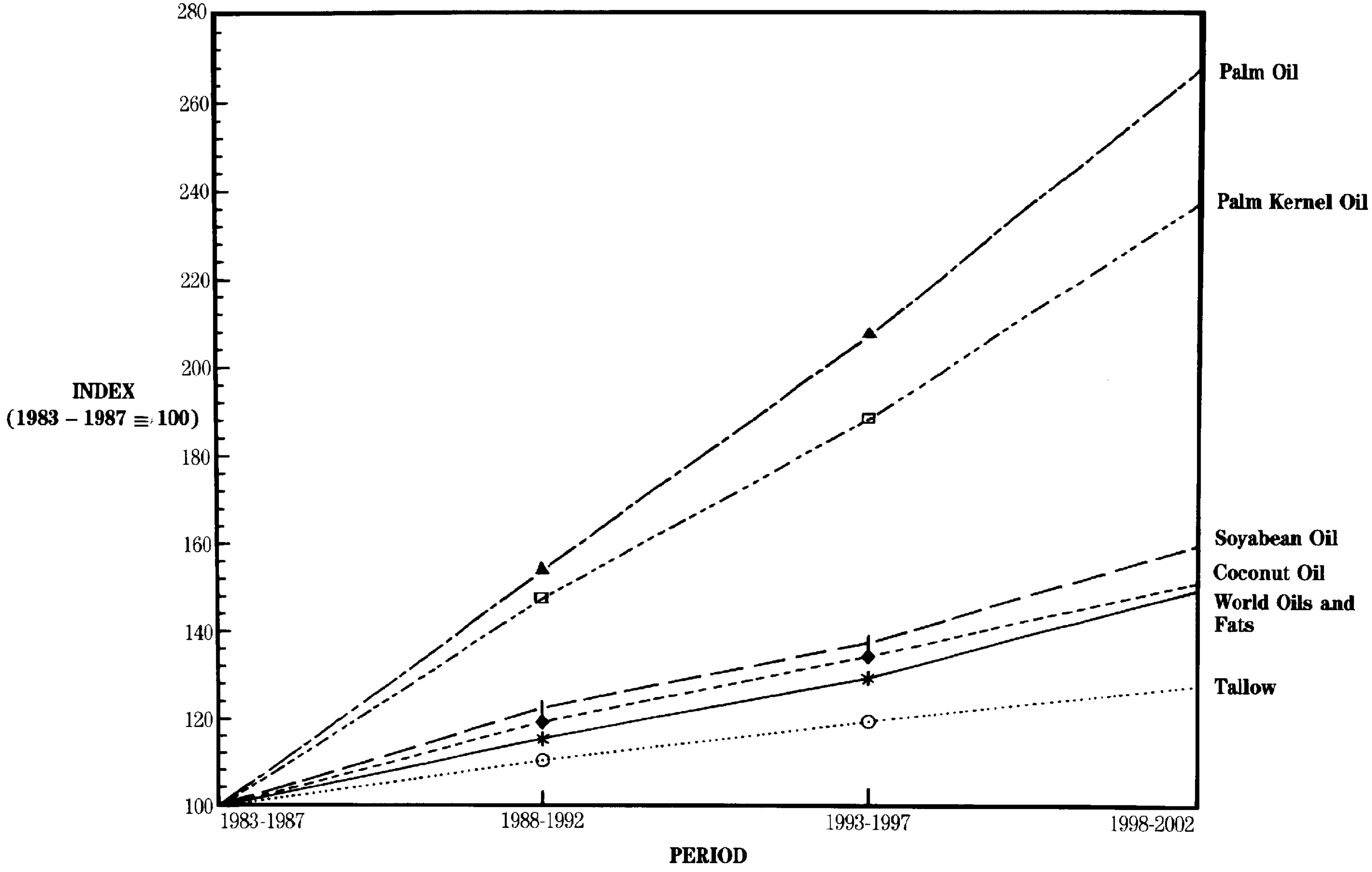

Figure 3.
Forecast of World Production

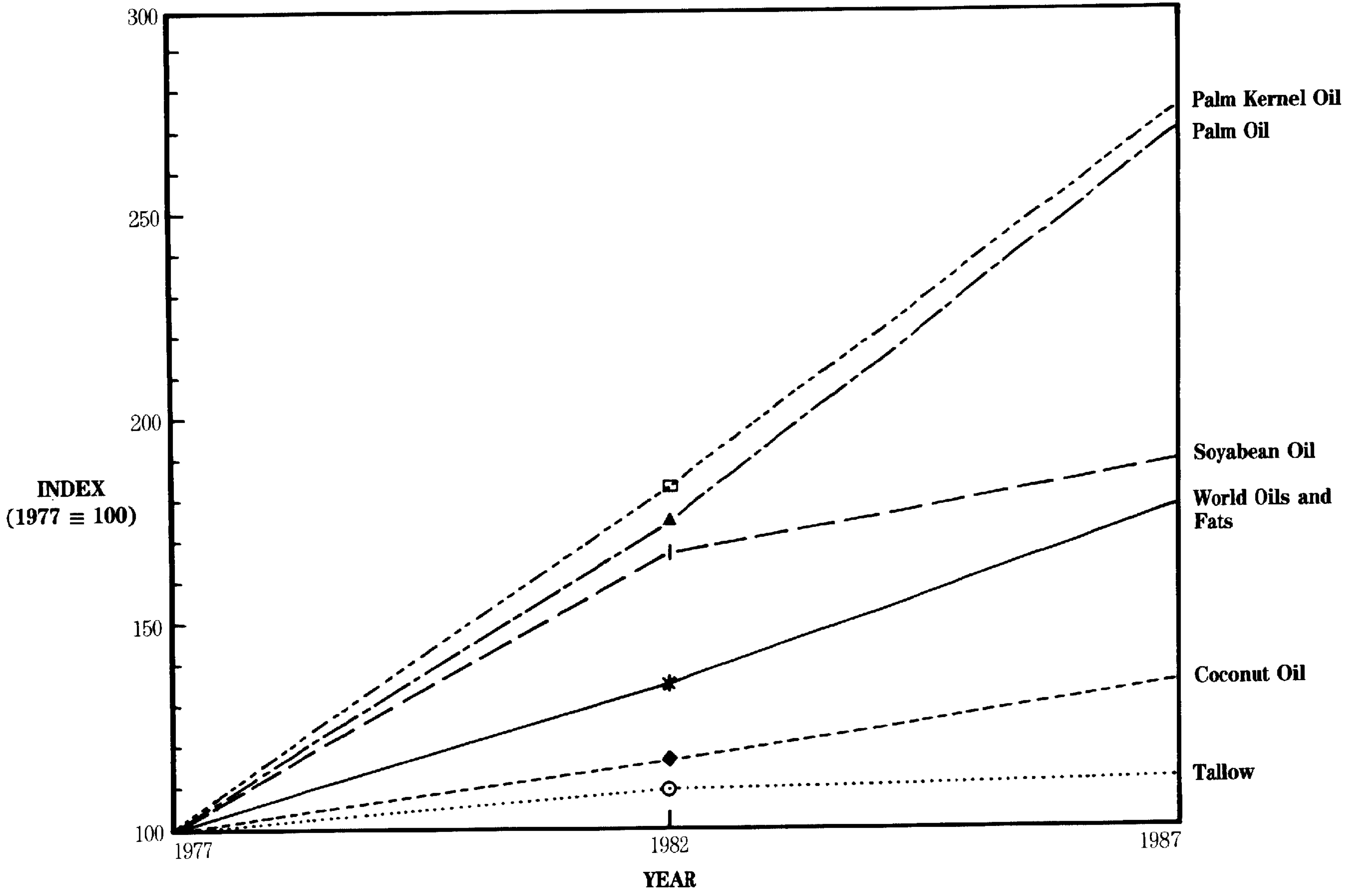

Figure 4.
World Exports of Oils and Fats

annual rates than all other oils and fats, while tallow and coconut oil production is expected to increase very slightly, remaining virtually static.

Price Competitiveness

Tallow prices are generally lower than those of other oils and fats. In the past the premium of crude palm oil over crude tallow has always been very high. However, with the increased production of palm oil, there has been a downward pressure on the prices of palm oil and other oils. Since 1986, the average price of crude tallow had been higher than that of crude palm oil and refined bleached and deodorized (RBD) palm stearin *(Figure 5).*

In the past the prices of coconut oil and palm kernel oil have been generally about the same. However, with the increased availability of palm kernel oil in the eighties, the price of palm kernel oil is now consistently lower than coconut oil *(Figure 6)*. This price advantage is becoming a major incentive for substitution of coconut oil by palm kernel oil.

The price differentials referred to above are based on CIF Rotterdam. Hence crude palm oil, RBD stearin and palm kernel oil offer a considerable price advantage over materials available in Rotterdam to oleochemical producers in Malaysia and other countries in the Association of South East Asia Nations (ASEAN).

FATTY ACIDS AND DERIVATIVES

Fatty Acids

The processing of crude palm oil and crude palm stearin into fatty acids involves pretreatment of the oils to remove impurities such as gums, soaps and solid matter. In the case of palm kernel oil, pretreatment is not necessary because this oil is relatively clean (Suan, *et al.*, 1985). The first important step in processing the oils is splitting or hydrolysis of the triglycerides to yield glycerol and a mixture of fatty acids. The hydrolysis can be done batchwise according to the Twitchell process or continuously at high temperature and pressure. Today, the Twitchell process is being phased out and the continuous process is almost the universal route for the production of fatty acids. This continuous countercurrent splitting process employs a temperature of 250°C-260°C and a pressure of 5.17 MPa (750 psi) and with a residence time of about two to three hours, a 98%-99% conversion of triglycerides to fatty acids can be achieved. The sweet water obtained has above 12%-20% of glycerol (Suan *et al.*, 1985; Combs, 1985; Sonntag, 1982; Sonntag, 1979).

The crude fatty acids can be used as they are. However, high-purity acids can be produced by simple distillation or fractionation. Distilled products retain the distribution of fatty acid chain length found in the original oils. One of the largest uses of these fatty acids is in the manufacture of soap and shampoos. The mixture of fatty acids may be fractionated to obtain individual fatty acids having more than 99% purity. However, the separation of saturated octadecanoic acid and unsaturated 9-octadecenoic acid by fractional distillation is not practised commercially. Other separation methods have to be used (Sonntag, 1979; Stage, 1984; Berger, *et al.*, 1979).

Fat splitting is a highly heat-dependent process. In efforts to reduce the heat requirement for this process, enzymatic hydrolysis has been investigated, and may offer the greatest hope of developing a low energy process for fat splitting (Sonntag 1984; Cheah *et al.*, 1987).

Fatty acids and derivatives find applications in various field. The following sections will discuss the use of fatty acids and derivatives in cosmetics, rubber applications, candles, water repellants, soaps and metallic soaps.

Direct Application

Cosmetics

Fatty acids find direct application in cosmetics. They are incorporated into many products such as shaving creams, hand and body lotions and hair colourants, for emollient and superfatting effect. Tetradecanoic, hexadecanoic, octadecanoic and 9-octadecenoic acids are used in shaving cream.

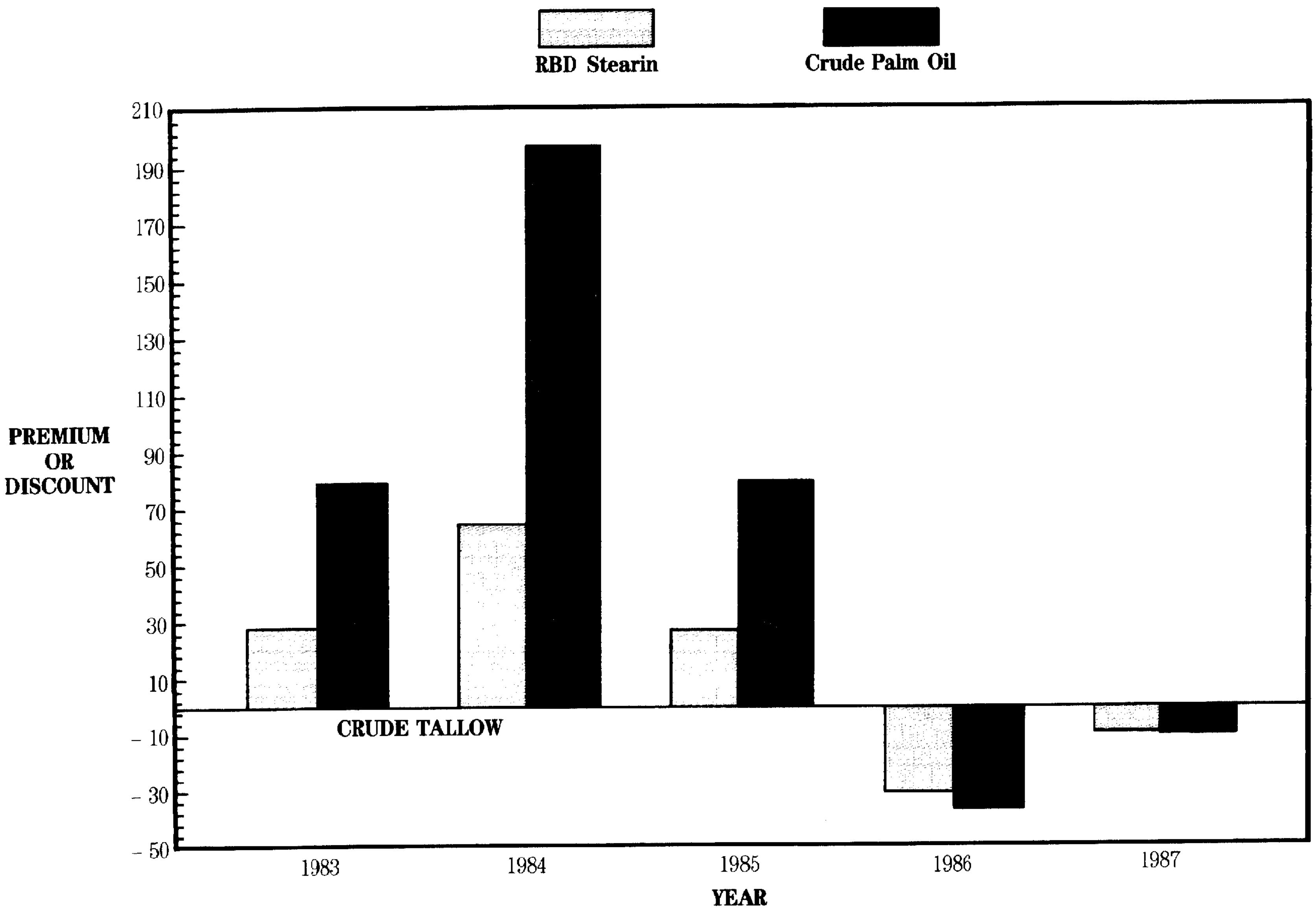

Figure 5.
Prices of RBD Palm Stearin and Crude Palm Oil vs Crude Tallow

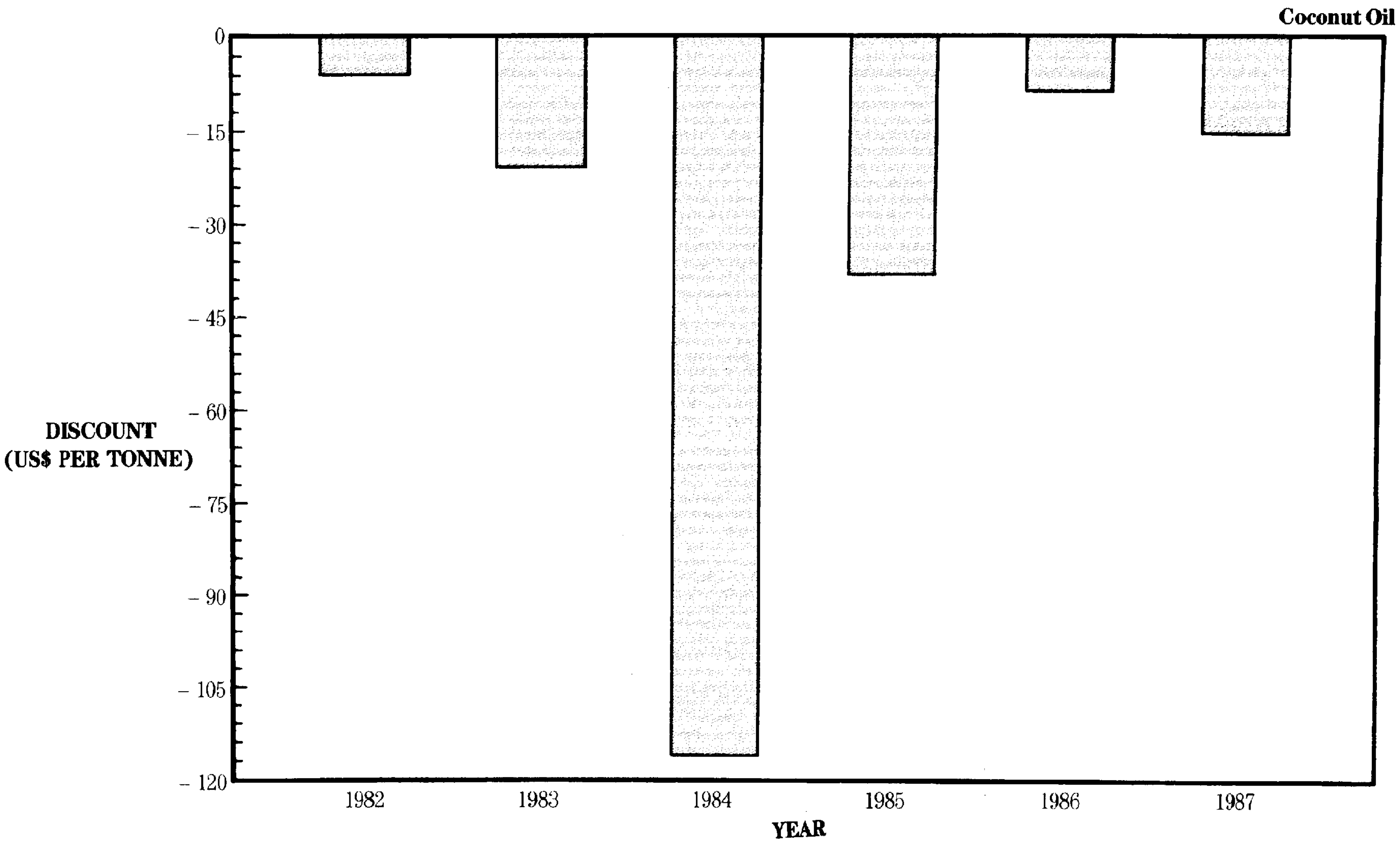

Figure 6.
Prices of Palm Kernel vs Coconut Oil

Octadecanoic acid is used to impart high lustre and sheen in hair conditioning. Octadecanoic and hexadecanoic acids are used in the preparation of foundation creams. The main type of fatty acid used in the cosmetic industry is a eutectic mixture of 45% octadecanoic acid and 55% hexadecanoic acid (Hamirin *et al.*, 1985; Johnson, 1978; Hutchison *et al.*, 1979).

Rubber Applications

The rubber industry uses a significant amount of fatty acids and their derivatives. Fatty acids are used as compounding aids and additives in rubber processing. They act as softeners and plasticizers when compounded into rubber so that the rubber formulation can be worked out more easily during mixing, calendaring, extrusion and moulding. The fatty acids also prevent the rubber sticking to the moulding equipment by acting as lubricants and release compounds.

Fatty acids are used during the vulcanization of both natural and synthetic rubber to maximize the utilization of sulphur. The type of fatty acid is not too important in this function and usually one is chosen based on its cost and availability. However, the unsaturation level must be low, usually less than 0.5%, as unsaturation would adversely affect the vulcanization process. Generally, rubber-grade octadecanoic acid is preferred over 9-octadecenoic acid because of its better resistance to oxidation (Hamirin *et al.*, 1985; Stage 1984).

Candles

The traditional raw materials used for making candles are beeswax and fats. After the development of fat splitting and the introduction of paraffin wax, paraffin wax and fatty acids supplanted solid fats in the manufacture of candles. Most modern candles contain approximately 5% - 30% octadecanoic acid with paraffin wax as the major component. The actual proportion is dependent upon the type of candle desired and its intended use. Due to the increasing cost of petroleum-based paraffin wax, octadecanoic acid has become increasingly attractive for candle making (Johnson, 1979; Weiss, 1979; De Vries, 1987). However, the use of a higher percentage of palm fatty acid in candle making poses some problems during processing, particularly because of the poor shrinkage and poor colour stability. Recent findings by the Palm Oil Research Institute of Malaysia (PORIM) indicated that the poor colour stability could easily be overcome by using a red dye which is relatively stable towards heat and light. It was also found that good shrinkage occurred when about 70% of palm fatty acid was incorporated into the wax. Hence good quality spiral candles can be made from palm fatty acids and paraffin wax in the ratio of 7:3 (Ooi *et al.*, 1987).

Water Repellants

Fatty acids and many of their derivatives possess water repellancy properties. Octadecanoic acid and its homologues have been used in many ways to confer water repellancy on many materials, *e.g.* waterproof agents for paper and textiles. Octadecanoic and hexadecanoic acids have generally been used, but also 9-octadecenoic and tetradecanoic acids.

The water repellancy of octadecanoic acid and its derivatives has also been applied to concrete for a slightly different end result. When applied to hardened concrete, they assist in minimizing cracking of the material when the temperature drops to below the freezing point, by repelling absorbed water. The potential for the use of octadecanoic acid and some of its derivatives in this area remains to be developed (Weiss, 1979).

Soap Making

About a third of the world's production of fatty acids goes into the manufacture of soaps. Traditionally soap is produced, along with 1,2,3-propanetriol, by the saponification of suitable oils and fats. The processing technology is relatively complex, particularly in terms of purifying the soap and recovering 1,2,3-propanetriol by countercurrent washing. Since the advent of continuous fat splitters, soaps have been predominantly produced from distilled fatty acids by neutralization. In this process, fatty acid is reacted with sodium hydroxide at 90°C — 100°C to liberate the sodium salt of the fatty acid (neat soap) and water.

Fatty acids can also be added in their unneutralized form to the neat soap as superfatting agents. This helps to improve the quality of the soap by interacting with the soap base to alter the structure of the lather. The number of large bubbles is decreased and the number of medium to small-sized bubbles is increased, which makes the lather thicker and more stable. Apart from lathering properties, superfatting also improves the feel of soap bars and imparts a beneficial mildness.

Palm-based fatty acids have already been well accepted by soap manufacturers to produce good quality toilet soaps (Hamirin *et al.*, 1988).

Metallic Soaps

Metallic soaps is the general term for the metallic salts of fatty acids other than sodium salts. They have an endless variety of applications. Octadecanoic acid metal salts (metal stearates) form the largest commercial class. Metal soaps find wide applications in the cosmetics and toiletries industry, the rubber industry, the plastics industry, the pharmaceutical industry and others. Commercially, metallic soaps are produced via two methods *i.e.* precipitation and non-aqueous fusion. Metal soaps are used as emulsifiers, thickening agents, foam stabilizers and emollients in the cosmetics industry. In the rubber industry, they are used as emulsifiers and stabilizers, *e.g.* in making styrene butadiene rubber, soap is used to disperse the ethenylbenzene (styrene) and butadiene into water before polymerization. In the plastics industry octadecanoic acid metal salts are important external and internal lubricants. Octadecanoic acid metal salts are used as lubricants in the manufacture of tablets. They are classified as catalysts or additives (Hamirin *et al.*, 1985).

Calcium soap is an important ingredient in animal feed as a supplement to the ruminant diet, which is normally fed to cattle, especially during lactation. It has been shown that performed calcium soaps in the cell walls of ruminants have higher digestibility than that of straight fats. Palm based calcium soaps have advantages due to the high content of palmitic acid, which is an important component cow's milk (Hamirin *et al.*, 1988).

METHYL ESTERS

Methyl esters of fatty acids can be manufactured either by direct esterification of fatty acids or by transesterification of triglycerides. The esterification can be carried out batchwise at 200°C—250°C under pressure. To obtain a high yield, the water of reaction has to be removed continuously. Esterification can also be done continuously in a counter-current reaction column using superheated-methanol (Kreutzer, 1984).

The predominant process for the manufacture of methyl esters is the transesterification of triglycerides with methanol. The methanolysis of naturally-occurring oils and fats with methanol takes place quite readily at a low temperature of about 50°C—70°C and at atmospheric pressure with an excess of methanol and in the presence of an alkaline catalyst such as sodium methoxide or sodium hydroxide (Sonntag, 1982; Kreutzer, 1984; Freedman *et al.*, 1984; Farris, 1979). These mild reaction conditions, however, require an oil neutralized by means of alkali refining, steam distillation or preesterification of free fatty acids. For the preesterification of free fatty acids in oils to form methyl esters, a number of solid catalysts have been used. The Lion Corporation of Japan used a special synthetic resin as catalyst. Oils containing free fatty acids are mixed with methanol and the free acids converted into methyl esters by continuous passage through the packed column of the catalyst resins (Ogoshi *et al.*, 1985). PORIM also used a solid catalyst to convert the free fatty acids of crude palm oil into methyl esters in its pilot plant for the production of methyl esters to be used as diesel substitute (Ong *et al.*, 1986; Choo *et al.* , 1986; 1987; 1987; 1988). The removal of free fatty acids is not required if the transesterification is carried out under pressure, *e.g.* at 9 MPa and at a higher temperature, *e.g.* at 240°C. Under these conditions, free fatty acids and triglycerides are converted into methyl esters simultaneously (Kreutzer, 1984).

Methyl esters, derived from palm oil and palm kernel oil, can be substituted for fatty acids as intermediate materials for the production of a number of fatty acid derivatives.

By using methyl esters as raw materials, several benefits may be realized, such as higher purity of finished products, milder processing conditions, and cheaper materials for construction. Methyl esters are also being used increasingly in fractional distillation because they have lower boiling points and are less corrosive than fatty acids (Sonntag, 1984; Farris, 1979).

The derivatives that are currently being made from methyl esters are fatty alkanolamides, fatty alcohols and isopropyl esters. Other derivatives which show good potential for the future are alpha-sulphonated methyl esters which can substitute for linear alkylbenzene sulphonate (LAS), sucrose polyesters and anhydrous soap. Another potential large application of methyl esters is as diesel fuel substitute.

Derivatives and Applications of Methyl Esters

Fatty Alcohols

The largest use for methyl esters is in the production of fatty alcohols by high pressure hydrogenation in the presence of a heterogeneous catalyst. Details will be discussed in the section on fatty alcohols.

Fatty Alkanolamides

Fatty alkanolamides can be produced from fatty acids or methyl esters. Fatty alkanolamides produced from fatty acids are low activity amides (typically 60%-65% active). Fatty amides produced from methyl esters are more than 90% active and often called 'super amides' (Farris,1979). The reaction of methyl esters and alkanolamines for the production of 'super amides' is carried out at 100°C-110°C and uses sodium methoxide as catalyst (Reck, 1985; Farris, 1979; Freedman, 1987). Diethanolamine accounts for the major percentage of all alkanolamines used for making alkanolamides (Farris, 1979). Alkanolamides are used in detergent foam boosters, thickening agents, emulsifying and wetting agents, plasticizers, anti-blocking agents for plastics, and germicides. The largest quantities are used by the detergent and cosmetic industries because the alkanolamides function as essentially nonionic surfactants capable of stabilizing foam and building viscosity. The superamides are preferred for shampoos and light duty liquids where their high purity makes them more efficient than the low activity alkanolamides. The low activity amides find application in hard surface cleaners because of their good solubility and detergency (Farris, 1979, Freedman, 1987).

Alpha-Sulphonated Methyl Esters

Alpha-sulphonated methyl esters, because of their wide-range of applications and biological properties, represent an interesting class of anionic surfactants. They are generally prepared from saturated fatty esters by reaction with sulphuric acid, oleum or sulphur trioxide, with or without halogenated solvents. After neutralization they form monometallic salts of sulphonated esters. In general, the saturated straight chain fatty acids having 12 to 18 carbon atoms, are of major commercial interest (Bluestein *et al.*, 1979).

Alpha-sulphonated methyl esters possess good washing and foaming properties, good biological degradability, good skin compatibility and low acute toxicity. They can be considered as surfactant components for phosphate-free or low-phosphate detergents. Alpha-sulphonated methyl esters also have other favourable technical properties which allow them to be used in cosmetics, as auxiliary agents in the production of fibres, plastics and rubber, and in leather manufacture (Stein *et al.*, 1975).

The chain lengths of those fatty acids with the highest washing power lie between C16 and C18 and as the order of excellence is C16 > C18 > C14 in terms of detergency and foaming, palm stearin, which is mainly composed of C16 and C18 acids, is most suitable as a raw material (Ogoshi *et al.*, 1985).

Soaps from Methyl Esters

Apart from the two common methods of producing soap, *i.e.* direct saponification of fats and neutralization of fatty acids, soap can also be produced by saponification of methyl esters as revealed in the USA in about 1940 (Bradshaw *et al.*, 1942; Bradshaw *et al.*, 1944; Bradshaw, 1942). A Japanese company, Lion

Corporation claims to have developed a process, the ES process, which produces good quality methyl esters for the manufacture of high quality toilet soaps on a large scale (Ogoshi *et al.*, 1985).

Methyl Esters as Alternative Diesel Fuels

Since 1970, considerable effort has been devoted to searching for an alternative to diesel fuel. Methyl esters have shown the greatest promise among all the possible candidates, *e.g.* microemulsions, blends of vegetable oils with diesel fuel and neat vegetable oil (Ziejewski *et al.*, 1984; Goering *et al.*, 1984; Clark *et al.*, 1984; Hawkins *et al.*, 1982; Quick *et al.*, 1982; Pischinger *et al.*, 1982).

In 1982, Malaysia, through PORIM, initiated an extensive programme to evaluate methyl esters of palm oil as a diesel fuel substitute. The preliminary field trial involving eight taxis (all with indirect injection engines) was successful: all the taxis completed 70 000 km and results were satisfactory. Subsequently, an exhaustive field trial involving a larger number and different types of diesel engines was launched and this the trial is still on-going (Ong *et al.*, 1986).

Although, at current prices, the use of methyl esters as a diesel fuel substitute is not economically viable, nevertheless it is important to establish the technology of using methyl esters as diesel fuel because vegetable oils and their derivatives are renewable whereas petroleum fuels will inevitably be depleted in the not too distant future.

FATTY ALCOHOLS

Fatty alcohols, synthetic or natural, form an important basic material for a wide variety of derivatives and applications. Today, there are three main processes for the production of fatty alcohols: the high-pressure hydrogenation of fatty acids and methyl esters, the Ziegler synthesis and the Oxo synthesis. The high-pressure hydrogenation of fatty acids and methyl esters produces natural alcohols from natural oils and fats. The Ziegler and Oxo processes produce synthetic alcohols from petrochemicals. Natural fatty alcohols of the C12-C14 range are obtained from coconut oil and palm kernel oils as primary feedstocks, and the C16-C18 range of natural fatty alcohols derive from tallow, palm oil or palm stearin as primary feedstocks.

Theoretically, triglycerides, fatty acids and methyl esters can be hydrogenated to fatty alcohols by using the high pressure hydrogenation process. The direct hydrogenation of oils and fats has not been developed into a commercial scale process, however, because it was not possible to prevent decomposition of the 1,2,3-propanetriol. The direct catalytic hydrogenation of fatty acids without pre-esterification requires corrosion-resistant materials for construction and acid-resistant catalysts (Kreutzer 1984). Lurgi has developed a catalytic hydrogenation process which allows the use of fatty acids as feedstock without pre-esterification (Voeste *et al.*, 1984, Buchold, 1983).

Most of the natural fatty alcohol plants use methyl esters as feedstock. Generally, the catalytic hydrogenation of methyl esters is carried out at 200°C - 300°C and 20-30 MPa with catalysts such as copper chromite, nickel or copper carbonates, or copper and chromium oxide (Monick, 1979). Saturated alcohols are obtained when copper containing catalysts are used in the hydrogenation process. However, the double bonds of the starting materials can be retained by using a selective catalyst, *e.g.* $Al_2O_3/CdO/Cr_2O_3$ (Kreutzer, 1984; Glasl, 1982).

Direct Applications of Fatty Alcohols

Most of the fatty alcohols are converted to derivatives, less than 5% being used in direct applications (Glasl, 1982). Two main areas of application can be distinguished based on chain length: C6-C10 fatty alcohols are mainly used as plasticizer raw materials, and the major use of C12-C18 fatty alcohols is in detergents. Hence, the C6-C10 fatty alcohols are commonly called the plasticizer range alcohols and the C12-C18 are called the detergent range alcohols (Monick, 1979; Glasl, 1982).

1-Octanol and 1-decanol are used as solvents in lacquers, printing inks, textile auxiliaries and pest control agents. In some applications, fatty alcohols act as foam-boosters and in others as foam depressants; *e.g.* 1-octanol is used as a foam-booster in flotation processes and C6-C10 fatty alcohols are used as foam depressants in aqueous drilling muds (Glasl, 1982). 1-Octanol and 1-decanol are used as tobacco sucker inhibitors (Hamirin *et al.*, 1985, Glasl, 1982).

C12-C14 fatty alcohols are used as lubricants in cold-rolling of aluminium. They are also used in bearing oils and hydraulic oil formulations. C16-C18 fatty alcohols are used as foam inhibitors. They are also used as consistency-giving agents, thickening agents and solubility retarders in cosmetic and pharmaceutical products. Other direct uses of C16-C18 fatty alcohols are as lubricants for processing plastics and as evaporation control agents for water reservoirs (Glasl, 1982).

9-Octadecenol-1 (oleyl alcohol) is used directly in creams and lotions in which it functions as an emollient and emulsion stabilizer. Due to good colour and low odour, it is also used in cosmetic emulsions (Egan *et al.*, 1984).

Fatty Alcohol Derivatives

The more important uses of fatty alcohols are as their derivatives such as fatty alcohol sulphates, fatty alcohol ethoxylates and fatty alcohol ether sulphates, which are widely used in the detergent and cosmetics industries.

Fatty Alcohol Sulphates

Fatty alcohol sulphates, especially those derived from coconut and palm kernel fatty alcohols, are the most important fatty alcohol derivatives in the detergent range. They are produced by reacting fatty alcohols with sulphating reagents such as sulphur trioxide, chlorosulphonic acid, 100% sulphuric acid or oleum (Glasl, 1982, Jungermann, 1979). To preserve the unsaturation present in the alcohol, sulphamic acid (NH_2SO_3H) is often used as sulphating agent (Hamirin *et al.*, 1985; Glasl, 1982). The resulting products are then neutralized, mainly with sodium hydroxide, ammonia or alkanolamines (generally mono or triethanolamine) (Glasl, 1982).

In general, fatty alcohol sulphates represent a class of surfactant with excellent detergency, wetting and foaming properties. They are widely used in liquid products such as heavy duty and light duty detergents, shampoos, bubble-bath formulations and rug shampoos (Hamirin *et al.*, 1985; Glasl, 1982; Jungermann, 1979).

Sodium salts of short-chain fatty alcohol sulphates (C8-C10) are mainly used as technical wetting agents in liquid detergent formulations, *e.g.* as wetting agents for electro-plating baths. They are also used as hydrotropic components in liquid detergents. The ammonium and alkanolamine salts of the C12-C14 fatty alcohol sulphates are extensively used for liquid shampoos and bubble-bath formulations. Sodium salts of C12-C14 fatty alcohol sulphates are used in cosmetic formulations but due to their limited water solubility they are mainly used for tube, cream and pearlized shampoos, paste or powder detergents, and foamers for tooth pastes. C16-C18 fatty alcohol sulphate is among the most promising alternative raw materials for light-duty and all-round detergents. Current applications are mainly in the textile industry and in heavy duty detergents (Hamirin *et al.*, 1985; Glasl, 1982). Cetyl-stearyl fatty alcohol suphate is used as an emulsifier for ointments and creams (Glasl, 1982).

Fatty Alcohol Ethoxylates

Fatty alcohol alkoxylates are produced by the reaction of fatty alcohol and ethylene oxide (EO) or propylene oxide, using an acidic or basic catalyst (*e.g.* boron trifluoride, potassium hydroxide) (Hamirin *et al.*, 1985, Glasl, 1982).

The fatty alcohol ethoxylates are the most important class of non-ionic surfactants. Ethoxylates of C8-C10 fatty alcohol with 3-6 moles EO possess good wetting properties and are readily soluble in water (Hamirin *et al.*, 1985, Glasl, 1982). They are mainly used as wetting and washing auxiliaries in the textile industry, as components in liquid, concentrated, mild washing agents and low temperature washing detergents, and as acid stable foaming agents for oil-drilling. The dodecyl (lauryl) fatty alcohol ethoxylates with 7-10 moles of EO possess very good wetting and washing properties at low and medium temperatures. The main applications are as light-duty liquid detergents and as textile auxiliaries. The

C16-C18 fatty alcohol ethoxylates are mainly used in detergent powder formulations, in the textile industry and as emulsifiers in technical and cosmetic-pharmaceutical applications (Glasl, 1982).

Fatty Alcohol Ether Sulphates

Fatty alcohol ether sulphates are manufactured by the ethoxylation of fatty alcohols, followed by sulphation using sulphur trioxide or chlorsulphonic acid. The reaction products are mainly neutralized with sodium hydroxide, ammonia or alkanolamines (Glasl, 1982)

Fatty alcohol ether sulphates have high foaming power and their alkali salts have unlimited water-solubility. They are largely unaffected by water hardness, and have good skin compatibility and emulsifying power. They show an unusual rheological behaviour, *i.e.* the ability to be thickened. With these properties, fatty alcohol ether sulphates find applications in shampoos and cosmetic baths, as manual dish washing liquid detergents, as emulsifiers for polymerization and as technical foaming agents (Hamirin *et al.*, 1985; Glasl, 1982).

FATTY AMINES

Fatty amines are classified as primary, secondary and tertiary, depending on the number of alkyl groups attached to the nitrogen atom. About 25% of fatty amines are used in direct application, and the rest as intermediates for the production of amine derivatives, which are found in literally hundreds of commercially used end-products (Richtler *et al.*, 1984). Almost all these uses depend on the cationic nature of the amine derivatives. The important amine derivatives are quaternary ammonium compounds (QAC), ampholytes and amine oxides, which are used as textile and fabric softeners, biocides, petroleum processing aids and in surfactant formulations (Richtler *et al.*, 1984; Reck,1979;1985).

Fatty amines and their derivatives are important because, apart from their cationic nature, they are basic and strongly absorbed on a wide variety of surfaces.

Nitriles

Most amines are produced from nitriles. The classical production route for nitriles is by the reaction of a fatty acid with anhydrous ammonia in batch or continuous processes. The reaction is run at 280°C - 360°C and frequently uses a metallic oxide catalyst such as zinc oxide or manganese acetate at 0.1%-0.25% by weight. The reaction can be considered as a simple dehydration of fatty acid ammonia soaps or amides (Reck,1979;1985, Billenstein *et al.*, 1984).

Hoechst has recently developed a one step process for making nitriles directly from oils and fats. The reaction is conducted at 230°C-290°C and at atmospheric pressure, and promoted by a special catalyst (Billenstein *et al.*, 1984).

Nitriles have no significant direct application and are only used as intermediates for the production of amines.

Primary Amines

There are many methods for preparing amines, but the most common industrial process for making primary amines is the batch or continuous catalytic hydrogenation of a nitrile. The reaction is promoted by nickel or cobalt catalysts such as the Raney types. Ammonia, trace alkali or metal soap and trace moisture are used to suppress the formation of secondary amines. Ammonia is the preferred suppressor. The reaction is run at 120°C—180°C and 2-10 MPa (Billenstein *et al.*, 1984).

Octadecyl amine (stearyl amine) is used as a hard rubber mould release agent and dodecylamine is used in reclaiming both natural and synthetic rubber (Reck,1979;1985). Primary amines and their salts are used as effective flotation agents, as anticaking and water-repellant agents, corrosion inhibitors, lubricating additives, in all stages of the petroleum industry, as bactericides and as fuel and gasoline additives (Reck,1979;1985; Billenstein *et al.*, 1984).

The largest segment of use of the primary amines is for the production of quaternary ammonium compounds, amphoterics, amine oxides, *etc.*, via their role in the production of tertiary amines.

Secondary Amines

Secondary amines are also manufactured by the catalytic hydrogenation of nitriles at about 200°C and above atmospheric pressure. Nickel, cobalt, and copper-chromite can be used as catalysts to promote the reaction (Billenstein *et al.*, 1984; Glankler 1979). Nickel catalysts are most widely used commercially, and generally the copper-chromite catalyst is used to retain unsaturation (Johnson, 1978; Bradshaw, 1942). The ammonia formed during the reaction must be removed continuously to ensure complete secondary amine formation (Reck, 1985; Glankler, 1979).

The secondary amines are mainly used as chemical intermediates. They are the basic source of the difatty dimethyl quaternary ammonium compounds, but have also been used as ingredients in textile aids (Billenstein *et al.*, 1984; Glankler, 1979).

Tertiary Amines

There are three types of tertiary amines (Billenstein *et al.*, 1984):

a) the symmetrical trifatty amines, where all the alkyl chains are statistically identical;

b) the asymmetrical methyl difatty amines and the dimethyl fatty amines; and

c) the amine-ethoxylate adducts, derived from primary or secondary amines by reaction with ethylene oxide.

Trifatty amines can be produced by catalytic hydrogenation of fatty nitriles at high temperature and low hydrogen pressure, and usually with a nickel catalyst. They may also be produced by reacting symmetrical secondary amines with fatty alcohols at 180°C-250°C and 0.7-1.4 MPa. Trifatty amines in the C8-C10 range (Glankler, 1979) are of commercial interest.

Methyl difatty amines or dimethyl fatty amines are produced by the reductive alkylation of secondary or primary amines with formaldehyde in the presence of nickel catalysts at moderate temperature and pressure. They are also produced by the reaction of a fatty alcohol with dimethylamine at elevated temperatures and moderate pressures in the presence of Cu, Cr or Co catalysts, and by the reaction of a nitrile or an alkyl halide with dimethyl-amine (Billenstein *et al.* 1984; Glankler, 1979).

The amine-alkoxylate adducts are produced by the reaction of primary and secondary amines with ethylene oxide, propylene oxide or mixtures thereof (Billenstein *et al.*, 1984).

Tertiary amines have many industrial applications. Trioctyl and tridecyl amines are used extensively in the recovery of metals (Hamirin *et al.*, 1985; Billenstein *et al.*, 1984; Glankler,1979). Alkyl dimethyl amines are used as catalysts for certain polymerization reactions, *e.g.* the production of polyesters of 1,4-benzene-dicarboxylic acid (terephthalic acid) by ester exchange, and the copolymerization of vinylidene fluoride with hexafluoropropene (Hamirin *et al.*, 1985; Glankler,1979). Their derivatives are used as additives in fuel and lubricating oils (Billenstein *et al.*, 1984; Glankler, 1979). Ethoxylated alkylamines are used as emulsifiers in neutral and acid solution, as foaming or frothing agents, as corrosion inhibitors, as emulsion breakers, as wetting agents, as mud-drilling additives, as levelling agents for dyes, and as textile finishing agents (Reck, 1985)

Tertiary amines are also extensively used as intermediates for the manufacture of surfactants such as quaternary ammonium compounds, amphoterics/ampholytes and amine oxides (Reck, 1985).

Derivatives of Fatty Amines
Quaternary Ammonium Compounds

Quaternary ammonium compounds (QAC) are manufactured by alkylation of primary, secondary and tertiary amines using 'quaternizing' agents such as methyl chloride, dimethylsulphate, benzyl chloride or ethylene oxide, in stainless steel or glass-lined equipment at temperatures between 80°C and 100°C (Reck, 1985; Billenstein *et al.*, 1984). Production is by batch or continuous processes and most of them use alcohol/water as solvent, *e.g.* isopropanol, and the products are marketed as solutions containing 50% to 75% active material (Billenstein *et al.*, 1984; Glankler, 1979). The products obtained with the different quaternizing agents have different properties and serve widely different markets. The quaternary ammonium compounds are commercially the most important of the cationic and amphoteric surfactants, having a 40% market share of this class of surfactants, and the most important class of QAC are the dimethyl difatty ammonium salts (Billenstein *et al.*, 1984).

The largest market of quaternary ammonium compounds is as fabric softeners dimethyl-di-octadecyl (dimethyldistearyl) ammonium chloride is the most important one. Other important uses are in the manufacture of organo-modified clays for the petroleum drilling industry, *e.g.* dimethyl dioctadecyl ammonium chloride and dimethyloctadecyl benzyl ammonium chloride, and in the bactericidal or sanitizer industries, *e.g.* dimethyl didodecyl ammonium chloride, dodecyl and tetradecyl dimethyl benzyl ammonium chloride and dodecyl and tetradecyl trimethyl ammonium salts (chloride and bromide). Other uses of quaternary ammonium compounds are as flotation agents for potash, silica and mica, as corrosion inhibitors in aqueous and oil systems, as dispersing agents in paints, as coating pigments, as adhesives between bitumen and road surfaces, as aids in sugar refining, *etc.* (Hamirin *et al.*, 1985; Reck, 1985; Billenstein *et al.*, 1984; Glankler, 1979).

CONCLUSION

Technically, almost all the oleochemicals which are currently produced from tallow and coconut oil can be produced from palm and palm kernel oils. Research and development work conducted by PORIM on oil palm hybridization with the aim of modifying the fatty acid composition of palm oil will further strengthen the position of palm oil and palm kernel oil as oleochemical feedstocks. The choice of raw material for oleochemical production will then be dependent on the availability and price competitiveness of the individual oils.

Over the last ten years, with a high annual rate of increase in production, palm and palm kernel oils have become important in the world oils and fats scene. This outstanding growth is expected to continue, and by the year 2000 palm and palm kernel oil will contribute about 40% of the total world export of oils and fats while the production of tallow and coconut oil is expected to be fairly static. Hence, one can be very sure that palm and palm kernel oils will be readily available despite the fact that a high percentage of palm oil will be used in food products.

As regards price competitiveness, palm stearin is competitive with crude tallow and palm kernel oil is very competitive with coconut oil.

The changes in the raw materials situation and in prices have increased the usage of palm stearin and palm kernel oil in the manufacture of oleochemicals and have also provided opportunities for expansion, relocation and diversification in the ASEAN region. Prior to 1980, less than 1% of the world's 75 oleochemicals were manufactured from palm and palm kernel oils but now the figure is estimated to be more than 10 per cent.

Hence, palm oil and palm kernel oil will pose a very strong challenge to the leadership in traditional raw materials and the ASEAN region will be significant to the oleochemical industry as it is the largest producer of palm oil, palm kernel oil and coconut oil.

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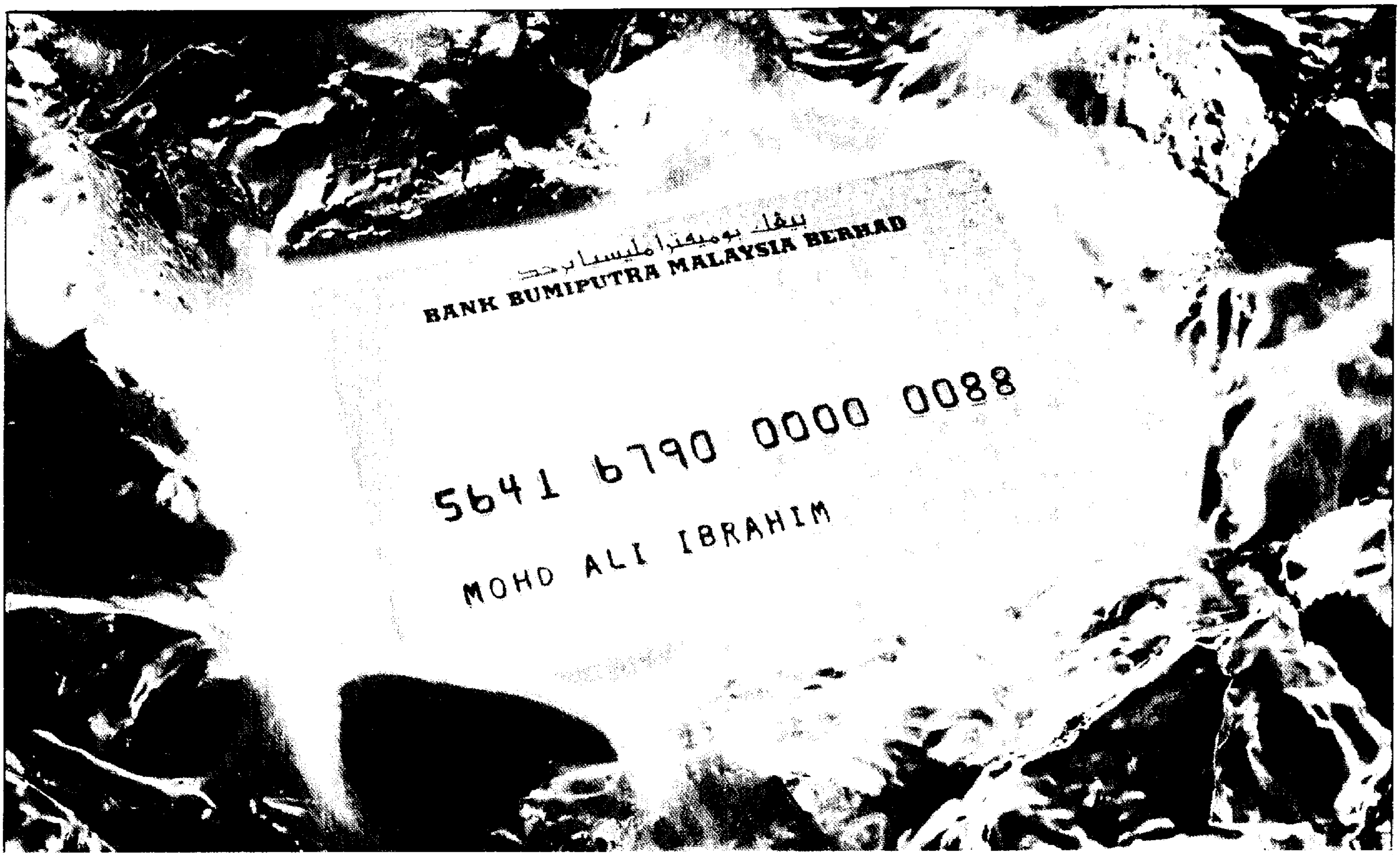
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